

VAPOR PRESSURE/BOILING POINT MEASUREMENTS
OF
SEVEN SELECTED ORGANIC SUBSTANCES

15.2.9

A Thesis Submitted
In Partial Fulfilment of the Requirements
For the Degree of
MASTER OF TECHNOLOGY

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by

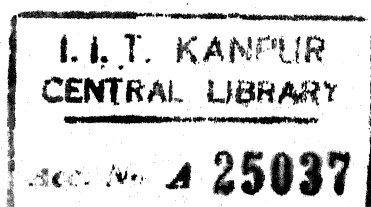
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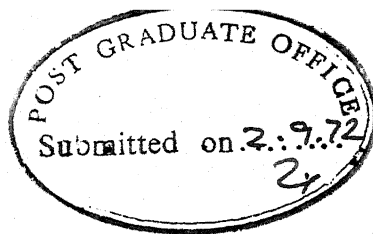
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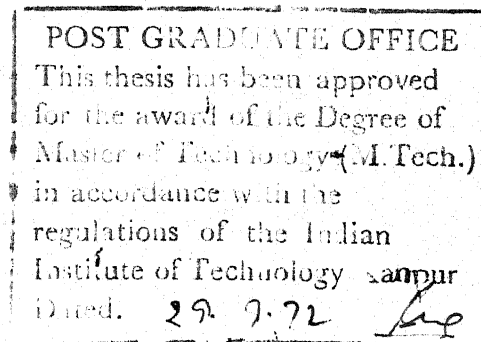
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CERTIFICATE

It is certified that this work has been carried out under my supervision and that this has not been submitted elsewhere for a degree.

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ABSTRACT

A twin ebulliometric technique has been used to measure the vapor pressure-boiling point data of Benzyl Benzoate, Bromoform, 1-Bromonaphthalene, Cycloheptane, Nonyl Alcohol (n-Nonanol), Nonyl Phenol, Propylene Trimer from about 90 to 900 mm Hg. pressure. Differential ebulliometers which enable the measurement of boiling and condensing temperatures at a particular pressure have been used. Water has been used as the reference compound. Temperatures are measured to an accuracy of $\pm 0.01^{\circ}\text{C}$ and pressures to ± 0.1 mm Hg. Literature data are available for Benzyl Benzoate, Bromoform, 1-Bromonaphthalene and Nonyl Alcohol, but the data are old and unreliable. Actual accuracy of temperature and pressure for each compound are reported. The data are fitted to the Antoine and Cox vapor pressure equations with good accuracy.

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CHAPTER 1

INTRODUCTION

Out of a very large number of organic substances synthesized so far, reliable experimental vapor pressure-boiling point data are available for at most one thousand substances. Much of this published information is available in the Thermodynamic Research Center compilations (18,19), Timmermans (24), Reid and Sherwood (16), Stull (20), Jordan (9), and Kanpur Critical Data Center compilation (10). Experimental methods of measurement are elegantly discussed by Hala, et.al. (6). In the present investigation, vapor pressure-boiling point measurements from 90 to 900 mm mercury pressure were carried out with Swietoslawski type differential ebulliometers described in detail by Osborne and Douslin (12). This method was selected over the static methods because at the pressures under consideration here, differential ebulliometry gives very precise and accurate results. In the ebulliometric apparatus, measurements are made by directly comparing the boiling temperature of the sample with the boiling temperature of a suitable reference substance, preferably water, in a common pressure manifold system blanketed with dry nitrogen. Temperatures were measured by copper-constantan thermocouples (3) calibrated against a Leeds and Northrup platinum resistance thermometer and K-3 potentiometer assembly. Pressures were roughly measured by a mercury manometer and accurately

calculated from boiling temperatures of the reference substance, water; the pressure value at each such temperature was calculated from the known vapor pressure-boiling point data of water (18). The accuracy of the temperature and pressure measurements were expected to be $\pm 0.02^{\circ}\text{C}$ and 0.1 mm Hg. respectively.

These vapor pressures are required in the prediction of vapor-liquid equilibria of multicomponent mixtures from the corresponding binaries. The compounds selected for the present investigation were partly based upon our vapor-liquid equilibrium studies and partly because some high purity compounds were available. The following compounds were studied:

1. Benzyl benzoate
2. Bromoform
3. 1-Bromonaphthalene
4. Cycloheptane
5. n-nonanol
6. Nonyl phenol
7. Propylene Trimer

Experimental data are available for benzyl benzoate (5), 1-bromonaphthalene (15), bromoform (14), and n-nonanol (20) but the data are old and unreliable.

The experimental data were fitted to the Antoine (23) and the Cox (4) equations. The Antoine equation is

$$\log_{10} P(\text{mm}) = A - \frac{B}{C + t(^{\circ}\text{C})} \quad (1)$$

The Antoine constants A, B, C were determined by a least squares regression (1) with optimization method by Rosenbrock search (17). The Antoine equation gives extremely good fit to the data in the range of 10 mm to 1500 mm Hg. pressure. The Cox equation

$$\log (P/760) = A_{\text{cox}} \left(1 - \frac{\text{BP}}{T^{\circ}\text{K}}\right) \quad (2)$$

$$\log A_{\text{cox}} = a + bT + cT^2$$

BP = normal boiling point, $^{\circ}\text{K}$

has been found to be better than the Antoine equation for fitting the data upto about 2000 mm Hg. pressure (4,12). The ideal ΔH_v values at the normal boiling point (at 760 mm Hg. pressure) were calculated by using Eqn.(1) and Eqn.(2) and the Clapeyron equation, Eqn.(3) assuming $v_g \gg v_l$.

$$\frac{dP}{dT} = \frac{\Delta H_v}{T \Delta v} = \frac{\Delta H_v}{T v_g} = \frac{\Delta H_v P}{RT^2} \quad (3)$$

The non-ideality correction could not be calculated because of the lack of necessary data.

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CHAPTER 2

EXPERIMENTAL APPARATUS

The experimental apparatus used in the present investigation is shown in Fig. 1. The differential ebulliometer shown in detail in Fig. 2. forms the heart of the apparatus. In this method, the boiling temperature of a substance is compared directly with that of water under nitrogen atmosphere.

Differential Ebulliometer: The ebulliometer used here is described by Osborne and Douslin (12) and is a modification of the one designed by Swietoslowski (21). As shown in Fig. 2, it consists of a boiler and condenser sections provided with re-entrant wells for measurement of boiling and condensing temperatures. The boiler 16 is a glass tube of 3 cm. dia. and 11 cm. long provided with a glass re-entrant well of 2 cm. dia. for the heater. The liquid in the boiler is heated by means of an electric heater placed in the well containing silicone fluid (Union Carbide) for a heat transmitting fluid. The heater is made of nichrome wire (24 gauge, 7.8 ohm/meter resistance) wound on a glass tube which is wrapped with asbestos cloth. Heat input to the heater is controlled through a variac. The heater is designed to cause necessary boiling rate corresponding to the desired pressure of the liquid. To promote steady boiling, the inner surface of the well exposed to the sample was provided with glass beads.

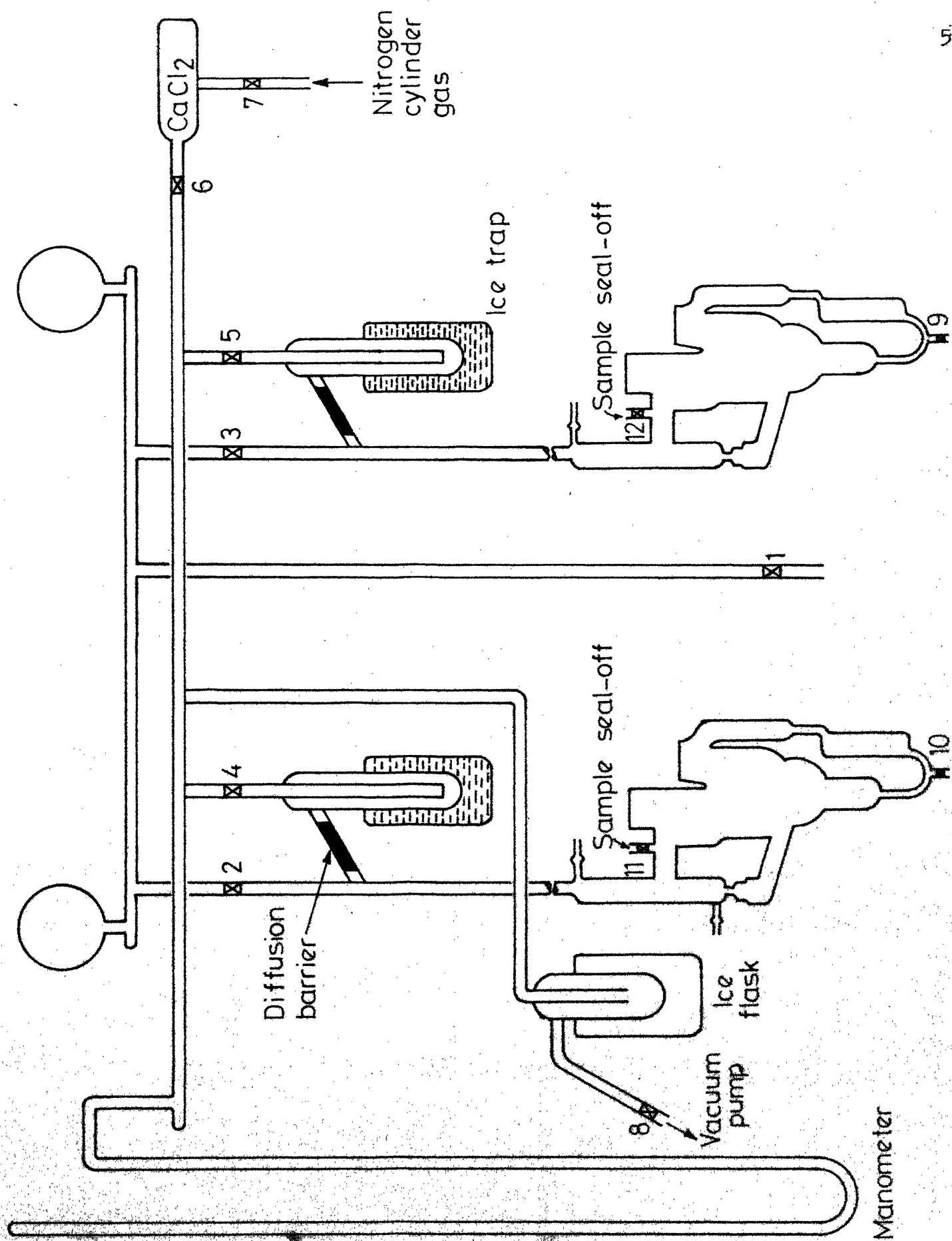


Fig.1 - Comparative ebulliometric vapor pressure apparatus.

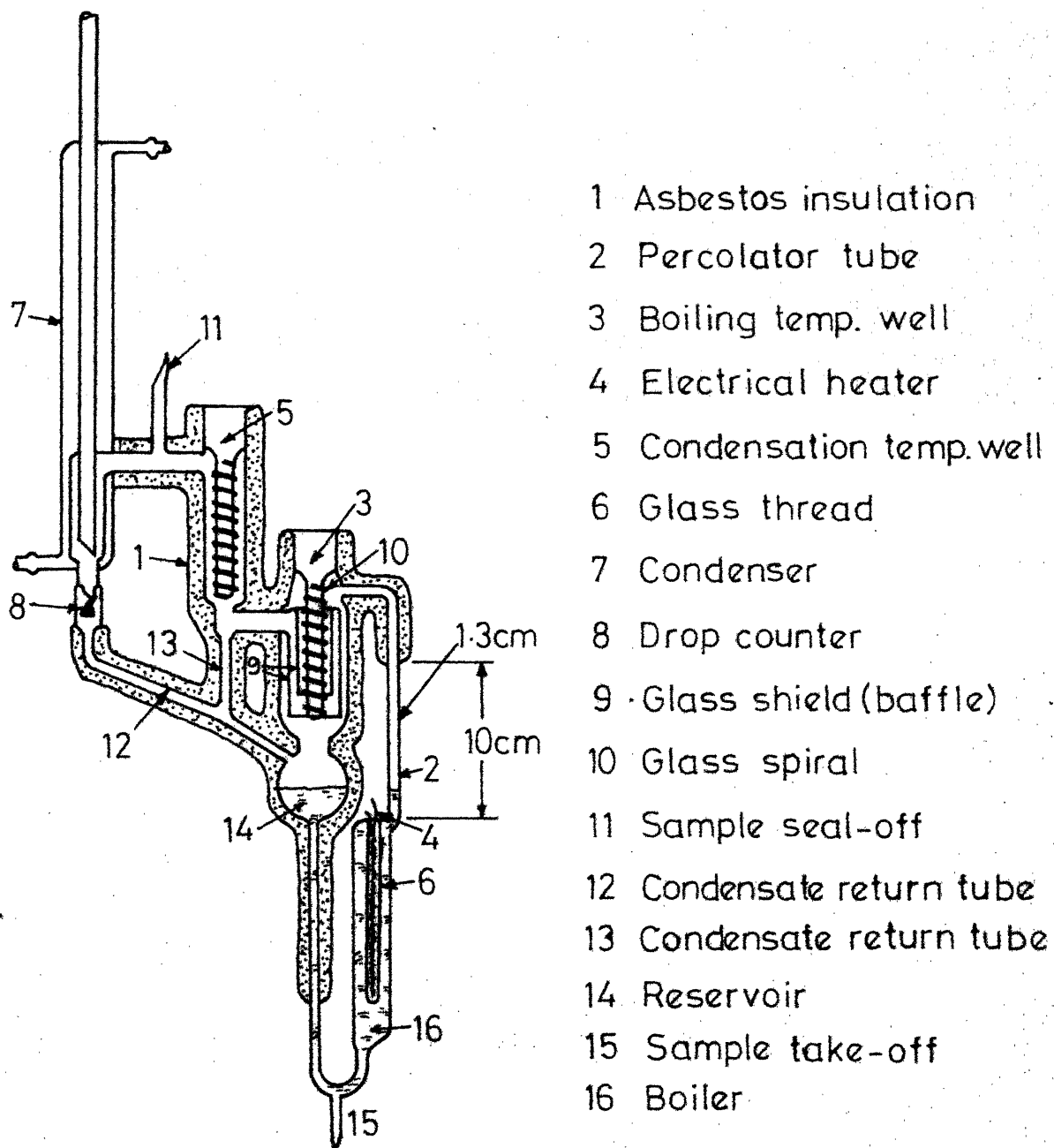


Fig. 2 - Differential Ebulliometer.

The boiler is connected to the condenser portion with a percolation tube, 2, of 1.3 cm. dia. and 16 cm. long. The ebulliometers are insulated to prevent heat loss, particularly around the thermometer wells. However, the percolation tube remained essentially uninsulated (top 5 cm was insulated), so that any superheat in the boiling liquid would be dissipated during its passage to the thermometer well, 3. The pure liquid vapor generated in the percolator tube enters the boiling temperature well, 3, where a part of it is condensed along the thermowell and into the reservoir, 14. The remaining vapor goes to the condensation temperature well, 5, where again part of it is condensed and enters the reservoir through the condensate return tube, 13. The uncondensed vapors next pass to the condenser, 7, and through the drop counter, 8, liquid finally returns to the reservoir through the return tube 12. This recycling proceeds until the equilibrium conditions - constancy of boiling and condensing temperatures - is attained. The difference in the boiling and condensing temperatures is a very good test of the purity of sample under investigation.

The thermometer wells 3 and 5 consist of 16 mm dia, 13 cm. long and 13 mm dia. 14 cm. long, tubes respectively provided with a glass spiral, 10, around it. The vapors enter the top of the spiral and travel to the bottom of the tube along the spiral thus providing intimate liquid-vapor

contact along the temperature well resulting in the measurement of "true" temperature.

Temperature Measurement: Temperatures are measured with a precision of 0.01°C by use of copper-constantan thermocouples(3) and a Honeywell potentiometer. The thermocouples were calibrated against a 25 ohm Leeds and Northrup platinum resistance thermometer and K-3 potentiometer assembly. The calibration details are given in Appendix A. Each thermocouple is placed in the thermowell containing silicone fluid for better heat transmission. The four thermocouples for four temperature measurements, boiling and condensing temperatures of sample and reference substance, are connected to a key from which two main leads are connected to the potentiometer for the measurement of voltage difference between the hot and the cold junctions. There was some difficulty with this arrangement and hence later single thermocouple was used to measure each temperature (as shown in Fig.4).

Pressure Measurement: The pressures are roughly measured in a long U-tube glass manometer, 10 mm i.d. and 15 mm o.d. containing triple distilled mercury. The manometer is approximately 1500 mm tall which fixes the maximum operating pressure in the system. The correct operating pressure in the system was calculated at the boiling temperature of the reference substance (equilibrium temperature) from Reference (18). The error in pressure measurement is expected to be 0.1 mm or

less.

As shown in Fig.1, each ebulliometer is connected to the manifold through a diffusion barrier-cold trap unit, and also to three glass ballasts one large and two small. The diffusion barrier consists of a sintered disc. The large ballast consists of one 40 liter flask enclosed in a wooden box to minimize the effect of outside temperature variation. It is connected to the system by a two-way glass stopcock, S1. Also, two small 4-liter flasks are similarly connected to the two ebulliometers through two-way stopcocks, S2 and S3, as shown in Fig.1. The function of the ballasts is to control and dampen the pressure fluctuations in the system.

A Cenco Hyvac vacuum pump is used for evacuating the system to 10^{-4} mm of Hg. Requisite pressure in the system is maintained by bleeding nitrogen gas from a nitrogen cylinder through a calcium chloride trap.

Each ebulliometer is provided with sample entry tube 11, a stopcock S11, with a ground glass joint, and a discharge tube with stopcock S10. The sample could be charged into the ebulliometer at S11 without contaminating it with air and moisture.

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CHAPTER 3

MATERIALS

1. Reference Substance Water:

Water was deionized, and distilled over potassium permanganate and sodium hydroxide to give a conductivity less than 1.0 micro-mho, in the Metallurgical Engineering Department, IIT/Kanpur. The effect of any impurities on the measured boiling temperatures was within $\pm 0.01^\circ\text{C}$. Water was selected as the reference standard because it can be made in very pure form and accurate and well recognized vapor pressure data are available for water.

2. Compounds Investigated:

n-Nonanol, bromoform, 1-bromonaphthalene, and cycloheptane were AR grade samples. These were used as such without further purification. Benzyl benzoate, nonyl phenol, and propylene trimer were lab reagent grade samples and were purified by fractional distillation in a 20 plate sieve column of 2.54 cm. i.d., at a 5:1 reflux ratio. Each sample purity was determined by density and refractive index measurements. The densities were measured at 37.82°C in a pycnometer (22) and a Bausch and Lomb Abbe refractometer type 33-45-58 (Sr.No.GD8646) was used to measure refractive index at 30°C . Table I gives the source, $d_4^{37.82}$ and n_D^{30} for each sample along with the literature values.

A rough calculation of sample purity was done using

TABLE I: PHYSICAL PROPERTIES OF MATERIALS

Compound	Source	Purity*	Present Value		Literature Value			
			B.P., °C	$d_4^{37.82}$ n_D^{30}	B.P., °C	d_4^{20} n_D^{20}	n_D^{21} for n_D^{21}	
Benzyl Benzoate	LR ^a	99.55	322.25	1.0283	1565	323.5(15)	1.1224(27) for d_4^{19}	1.5681(27) for n_D^{21}
Bromoform	AR ^b	99.96	148.63	2.6116	1,560	149.55(15)	2.8905(5)	1.5890(26)
1-Bromonaphthalene	AR ^c	99.88	292.74	1.3741	1.653	281.2(2)	1.4834(8)	1.66009(2) for n_D^{15}
Cycloheptane	AR ^d	99.97	119.35	0.7448	1.442	118.0(26) at 726 mmHg	0.8099(26)	1.4445(26)
n-Nonanol	LR ^e	99.81	215.20	0.7558	1.430	213.5(20)	0.8279(20)	1.4311(20)
Propylene Trimer	LR ^f	99.65	136.35	0.6701	1.420	-	-	-

*Estimated only (see text)

^aKelkar, India^bReachim, USSR^cHungary^dFluka, A.G. Bucks SG, Switzerland^eAldrich, USA^fAniline Dyestuffs, India

the following formula (11) which is based upon the elevation of boiling point in presence of an impurity.

$$X_B = \frac{\Delta H_v (T_b - T_o)}{RT_o^2} \quad (4)$$

where X_B = mole fraction of the impurity

ΔH_v = enthalpy of vaporization taken at $\frac{T_b + T_o}{2}$, cal/mole

T_b = boiling point of the impurity

T_o = boiling point of pure compound

R = Gas constant, 1.98717 cal.g.mole⁻¹

The $(T_b - T_o)$ value was taken as the difference between the boiling and condensing temperatures. T_o was calculated from the experimental vapor pressure data using the Antoine equation.

ΔH_v value was calculated at T_b using the Antoine constants and the Clapeyron equation assuming vapor phase ideality. In this manner the purity of each sample was determined and is reported in Table 1.

CHAPTER 4

EXPERIMENTAL PROCEDURE

With reference to Fig. 1, the system was tested for leaks after proper greasing of the stopcocks, etc. Once this was done, the following experimental procedure was followed to obtain the vapor pressure-boiling point data.

1. The whole system was cleaned with acetone and distilled water and dried.
2. S6, S9, S10, S11, S12 were closed and S1, S2, S3, S4, S5 and S8 were opened.
3. The system was evacuated for about 3-4 hours to 10^{-4} mm Hg. (as tested by McLeod gage). S8 was closed to again check leaks in the system.
4. If no leak, S2, S3, S4 and S5 were closed, the sample and water were filled into the respective ebulliometers through S11 and S12 from the small sample cylinders (50 cm^3) without exposing the samples to air and moisture. This was done in the following manner. The sample bottle stopcocks was closed and the bottle was attached to the ground-glass joint at S11. S11 was opened to evacuate the space between S11 and the sample bottle stopcock. The latter was slowly opened after starting the condenser water. The ebulliometer was thus filled by the required amount of

the sample. This procedure was also followed for charging water to the ebulliometer.

5. The lowest operating pressure was adjusted in the system by slowly bleeding dry N_2 gas through S7 and S6. The lowest operating pressure was fixed by the room temperature and the vapor pressure of water. S1 was kept open during an experiment for minimizing pressure fluctuations.
6. After the pressure adjustment was made slow heating was provided to the sample and water. This slow heating avoided any bumping. After some time, smooth boiling was observed. The boiling and condensing temperatures were noted every 10 minutes. It took on the average about 3-4 hours to reach equilibrium i.e. the boiling and condensing temperatures remained constant. The equilibrium pressure on the manometer, boiling and condensing temperatures of sample and water were noted.
7. The pressure was increased to a suitable value approximately 50 mm higher each time and the whole procedure i.e. No.5 and No.6-above was repeated.
8. In this fashion the entire pressure range was covered, the highest operating pressure being

about 1000 mm Hg. At about 1200 mm Hg., stop-cocks started blowing out and hence higher pressures could not be studied.

9. After completion of this work, sample and water were removed, the system cleaned and dried and the experiment was ready for another sample.

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CHAPTER 5

RESULTS

The experimental results are reported in Table II to VIII. Columns 2 and 4 are the average of the boiling and condensing well millivolt readings. Columns 3 and 5 are the temperatures obtained from the calibration results at each millivolt reading. Column 6 gives the system pressure calculated at water boiling temperatures as given in Column 5, using the Antoine constants from Reference (18). The temperatures reported in column 3 are given to more significant figures than the accuracy demands. The vapor pressure-boiling point data as given in columns 3 and 6 were fitted to the Antoine equation, Eqn.(1) and the Cox equation, Eqn.(2) by the least squares regression and optimization technique on IBM 7044 computer. The flow chart and the complete program is given in Appendix B. Columns 7,8,9 in Tables II to VIII give the deviations in temperature and pressure from the experimental data using the Antoine and the Cox equations. The Antoine and the Cox constants are also reported in the above tables along with the standard deviations of the fit. The H_v values reported in the above tables at the normal boiling point were calculated using Eqn.(3) as follows:

Antoine Equation:

$$\Delta H_v = \frac{2.302585 \text{ RB } (t + 273.15)^2}{(C + t)^2} \quad (5)$$

TABLE II

EXPERIMENTAL VAPOR PRESSURE-BOILING POINT DATA FOR

BENZYL BENZOATE

Antoine constants $A = 6.41969$ $B = 1588.81$ $C = 125.71$
 Cox constants $a = 1.36262$ $b = -2.22319 \times 10^{-3}$ $c = 1.79978 \times 10^{-6}$

Normal Boiling Point(B.P.) = $323.25^\circ\text{C} = 596.40^\circ\text{K}$

No.	Sample		Water		Pressure mm. Hg.	$\Delta t(^{\circ}\text{C})$		$\Delta P(\text{mm. Hg.})$	
	emf(mV)	t($^{\circ}\text{C}$)	emf(mV)	t($^{\circ}\text{C}$)		Antoine	Cox		
1.	11.245	224.701	1.8775	46.253	76.66	-0.076	0.18	-0.03	
2.	11.545	229.516	1.9995	49.084	88.42	-0.034	0.09	-0.01	
3.	12.955	251.635	2.5595	61.832	162.59	0.171	-0.71	-0.41	
4.	13.155	254.708	2.6405	63.644	176.53	0.332	-1.48	-1.15	
5.	13.645	262.170	2.8125	67.465	209.31	-0.261	1.33	1.65	
6.	13.765	263.984	2.8665	68.658	220.54	0.083	-0.44	-0.14	
7.	14.395	273.422	3.0995	73.766	274.58	-0.035	0.22	0.37	
8.	14.605	276.536	3.1785	75.484	295.09	0.013	-0.09	-0.02	
9.	14.725	278.309	3.2215	76.417	306.76	-0.038	0.26	0.27	
10.	14.835	279.930	3.2625	77.303	318.21	-0.016	0.11	0.07	
11.	15.235	285.788	3.4045	80.362	360.51	-0.184	1.43	1.18	
12.	15.875	295.053	3.6385	85.355	439.68	-0.058	0.52	-0.14	
13.	16.615	305.603	3.9005	90.880	543.72	-0.075	0.80	-0.13	
14.	17.365	316.126	4.1645	96.378	666.88	0.037	-0.46	-1.19	
15.	17.645	320.013	4.2595	98.341	716.10	-0.017	0.22	-0.19	
16.	18.025	325.252	4.3905	101.033	788.48	0.035	-0.49	-0.16	
17.	18.305	329.087	4.4875	103.016	845.59	0.121	-4.81	-0.68	

Std. Dev.

Antoine

Cox

P, mm Hg

t, $^{\circ}\text{C}$ ΔH_v , Kcal g-mole $^{-1}$
at B.P.

0.82

0.13

12.83

0.68

12.97

TABLE III

EXPERIMENTAL VAPOR PRESSURE-BOILING POINT DATA FOR BROMFORM

Antoine Constants $A = 8.46420$ $B = 1978.29$ $C = 205.69$
 Cox constants $a = 1.30579$ $b = -2.19405 \times 10^{-3}$ $c = 2.49238 \times 10^{-6}$
 Normal Boiling Point = $148.63^\circ\text{C} = 421.78^\circ\text{K}$

No.	Sample		Water		Pressure mm. Hg.	$\Delta t(^{\circ}\text{C})$ Antoine	$\Delta P(\text{mmHg})$ Antoine	$\Delta P(\text{mm Hg})$ Cox
	emf. (mV)	t($^{\circ}\text{C}$)	emf. (mV)	t($^{\circ}\text{C}$)				
1.	4.7775	108.894	2.4805	60.057	149.85	0.000	-0.01	-0.03
2.	5.0835	115.017	2.7535	66.158	197.56	0.001	-0.01	0.09
3.	5.4405	122.061	3.0735	73.199	268.07	-0.000	-0.00	0.16
4.	5.7905	128.867	3.3885	80.018	355.54	-0.010	0.14	0.23
5.	6.0075	133.040	3.5855	84.229	420.66	0.003	-0.05	-0.05
6.	6.0925	134.664	3.6625	85.864	448.51	0.000	-0.01	-0.05
7.	6.2055	136.816	3.7655	88.042	487.97	0.007	-0.14	-0.23
8.	6.2225	137.138	3.7805	88.358	493.94	-0.002	0.05	-0.06
9.	6.2785	138.201	3.8315	89.432	514.64	-0.002	0.03	-0.09
10.	6.4855	142.107	4.0205	93.388	597.31	0.003	-0.08	-0.26
11.	6.5985	144.226	4.1235	95.529	646.41	-0.003	0.06	-0.11
12.	6.7505	147.063	4.2625	98.402	717.70	-0.007	-0.19	0.09
13.	6.9305	150.401	4.4285	101.810	810.4	0.007	-0.21	-0.04

Std. Dev.

Antoine

Cox

P, mm Hg.

t, $^{\circ}\text{C}$ ΔH_v , Kcal g-mole $^{-1}$
at B.P.

0.10

0.005

12.83

0.13

12.86

TABLE IV

EXPERIMENTAL VAPOR PRESSURE-BOILING POINT DATA FOR 1-BROMONAPHTHALENE

Antoine Constants $A = 5.38175$ $B = 929.64$ $C = 91.06$
 Cox Constants $a = 1.06861$ $b = -1.39254 \times 10^{-3}$ $c = 8.90447 \times 10^{-7}$

Normal Boiling Point(BP) = $280.66^\circ\text{C} = 553.81^\circ\text{K}$

No.	Sample		Water		Pressure mm Hg.	$\Delta t(^{\circ}\text{C})$		$\Delta P(\text{mm Hg})$	
	emf (mV)	t($^{\circ}\text{C}$)	emf (mV)	t($^{\circ}\text{C}$)		Antoine	Cox		
1.	9.5245	196.274	2.4165	58.614	140.12	0.013	-0.05	0.03	
2.	10.535	213.142	2.8235	67.709	211.56	-0.033	0.16	0.06	
3.	11.455	228.076	3.1755	75.419	294.29	-0.003	-0.02	0.13	
4.	11.855	234.450	3.3225	78.598	335.58	-0.001	0.00	-0.08	
5.	12.495	244.509	3.5515	83.505	408.81	0.013	-0.10	-0.10	
6.	12.535	245.132	3.5655	83.804	413.66	0.012	-0.09	-0.09	
7.	12.895	250.710	3.6905	86.457	458.98	-0.015	-0.12	-0.07	
8.	13.255	256.238	3.8125	89.032	506.85	-0.012	0.10	0.20	
9.	13.685	262.776	3.9565	92.052	568.24	-0.014	-0.14	-0.01	
10.	14.525	275.351	4.2265	97.660	698.69	-0.045	-0.50	0.59	
11.	14.805	279.488	4.3155	99.493	746.39	-0.006	-0.07	-0.04	
12.	14.935	281.399	4.3555	100.315	768.62	-0.013	-0.16	0.14	
13.	15.115	284.036	4.4115	101.463	800.59	0.009	-0.11	-0.19	
14.	15.245	285.934	4.4515	102.281	824.04	0.019	-0.24	-0.37	
Std. Dev.					Antoine	Cox			
P, mm. Hg.					0.18	0.21			
t, $^{\circ}\text{C}$					0.019	-			
ΔH_v , Kcal g-mole $^{-1}$ at B.P.					9.44	9.43			

TABLE V

EXPERIMENTAL VAPOR PRESSURE-BOILING POINT DATA FOR CYCLOHEPTANE

Antoine Constants $A = 7.62501$ $B = 1877.90$ $C = 276.54$
 Cox Constants $a = 0.775148$ $b = -5.98439 \times 10^{-4}$ $c = 8.05657 \times 10^{-7}$
 Normal Boiling Point (B.P.) = $119.35^\circ\text{C} = 392.50^\circ\text{K}$

No.	Sample		Water		Pressure mm. Hg.	$\Delta t(^{\circ}\text{C})$	$\Delta P(\text{mm. Hg.})$		Cox
	emf.t. (mV)	t($^{\circ}\text{C}$)	emf (mV)	t($^{\circ}\text{C}$)			Antoine	Antoine	
1.	2.3935	58.094	2.1355	52.216	103.22	-0.038	-0.15	-0.23	
2.	2.8435	68.130	2.4815	60.079	150.00	-0.048	0.26	0.34	
3.	3.4935	82.268	2.9815	71.186	246.04	-0.014	0.12	0.28	
4.	3.8655	90.146	3.2645	77.346	318.78	-0.012	0.12	0.22	
5.	4.2845	98.856	3.5815	84.144	419.26	-0.000	0.01	-0.04	
6.	4.4545	102.342	3.7095	86.859	466.20	0.004	-0.06	-0.17	
7.	4.5795	104.889	3.8035	88.842	503.19	0.010	-0.15	-0.31	
8.	4.9355	112.066	4.0705	94.428	620.80	0.033	-0.59	-0.80	
9.	5.0115	113.593	4.1265	95.591	647.95	0.016	-0.30	-0.49	
10.	5.0545	114.440	4.1585	96.254	663.87	0.016	-0.30	-0.49	
11.	5.3265	119.823	4.3605	100.417	771.43	0.015	-0.37	-0.20	
12.	5.3855	120.983	4.4045	101.319	796.54	-0.022	-0.49	-0.38	
13.	5.5665	124.522	4.5345	103.973	874.37	-0.080	1.88	2.34	

Std. Dev.
 P, mm. Hg.
 t, $^{\circ}\text{C}$
 ΔH_v , Kcal g-mole $^{-1}$
 at B.P.

Antoine
 Cox

0.59
 0.75
 -
 8.47

TABLE VI

EXPERIMENTAL VAPOR PRESSURE-BOILING POINT DATA FOR

NONYL ALCOHOL (n-NONANOL)

Antoine Constants $A = 7.02986$ $B = 1705.94$ $C = 195.97$
 Cox Constants $a = 0.85997$ $b = -5.04744 \times 10^{-4}$ $c = 3.30039 \times 10^{-7}$

Normal Boiling Point(B.P.) = $215.20^\circ\text{C} = 488.35^\circ\text{K}$

No.	Sample		Water		Pressure (mm. Hg.)	$\Delta t(^{\circ}\text{C})$ Antoine	ΔP (mm. Hg) Antoine	ΔP (mm Hg) Cox
	emf. (mV)	t($^{\circ}\text{C}$)	emf(mV)	t($^{\circ}\text{C}$)				
1.	6.1385	135.541	1.8765	46.230	76.56	0.010	-0.03	-0.01
2.	6.8515	148.939	2.2815	55.553	121.26	-0.003	0.01	-0.03
3.	7.6975	164.387	2.7535	66.158	197.56	-0.008	0.05	-0.00
4.	4.1445	172.366	2.9995	71.581	250.23	-0.001	0.01	-0.02
5.	8.4385	177.550	3.1585	75.049	289.79	-0.046	0.38	0.37
6.	8.6515	181.274	3.2765	77.606	322.20	0.033	-0.29	-0.28
7.	8.9748	186.874	3.4495	81.327	374.79	-0.005	0.06	0.11
8.	9.2165	191.029	3.5795	84.102	418.55	0.003	-0.03	0.04
9.	9.6185	197.865	3.7935	88.632	499.15	0.000	-0.00	0.01
10.	9.8255	201.352	3.9035	90.943	545.02	0.015	-0.20	0.09
11.	10.425	211.331	4.2185	97.494	694.53	0.025	-0.41	-0.51
12.	10.755	216.749	4.3895	101.012	787.91	0.005	-0.09	-0.13
13.	10.995	220.657	4.5135	103.546	861.42	0.002	-0.03	-0.17
14.	11.265	225.023	4.6515	106.349	949.27	-0.028	0.60	0.29

Std. Dev.

Antoine

Cox

P, mm.Hg.

0.18

t, $^{\circ}\text{C}$

0.019

-

 ΔH_v , Kcal g-mole $^{-1}$
at B.P.

11.01

11.0

TABLE VII

EXPERIMENTAL VAPOR PRESSURE-BOILING POINT DATA FOR NONYL PHENOL

Antoine Constants $A = 7.74950$ $B = 2550.67$ $C = 206.28$
 Cox Constants $a = 0.90034$ $b = 4.64282 \times 10^{-4}$ $c = 3.26239 \times 10^{-7}$
 Normal Boiling Point(B.P.) = $317.61^\circ\text{C} = 590.76^\circ\text{K}$

No.	Sample		Water		Pressure mm.Hg.	$\Delta t(^{\circ}\text{C})$		$\Delta P(\text{mm.Hg.})$	
	emf (mV)	t($^{\circ}\text{C}$)	emf(mV)	t($^{\circ}\text{C}$)		Antoine	Cox		
1.	10.635	214.785	1.5185	37.804	49.18	-0.005	0.01	-0.01	-0.01
2.	12.935	251.327	2.4815	60.080	150.00	0.044	-0.18	-0.14	-0.14
3.	13.625	261.868	2.7665	66.447	200.11	0.016	-0.09	-0.04	-0.04
4.	14.485	274.758	3.1185	74.180	279.40	-0.076	0.54	0.57	0.57
5.	15.095	283.744	3.3705	79.632	350.00	-0.022	0.19	0.19	0.19
6.	15.475	289.278	3.5265	82.972	400.26	-0.009	0.09	0.07	0.07
7.	16.135	298.779	3.7955	88.674	499.96	-0.032	0.37	0.32	0.32
8.	16.485	303.762	3.9455	91.738	561.59	-0.084	-1.07	-1.13	-1.13
9.	16.765	307.721	4.0525	94.054	612.26	-0.019	-0.25	0.19	0.19
10.	16.985	310.815	4.1425	95.923	655.87	0.001	-0.01	-0.07	-0.07
11.	17.225	314.174	4.2425	97.990	707.09	0.088	-1.35	-1.38	-1.38
12.	17.435	317.100	4.3245	99.678	751.34	-0.022	0.33	0.35	0.35
13.	17.775	321.810	4.4615	102.485	829.98	-0.048	0.84	0.90	0.90

Std. Dev.

Antoine

Cox

P, mm. Hg.

0.59

t, $^{\circ}\text{C}$

0.046

 ΔH_v , Kcal g-mole⁻¹
at B.P.

14.85

TABLE VIII

EXPERIMENTAL VAPOR PRESSURE-BOILING POINT DATA FOR PROPYLENE TRIMER

Antoine Constants $A = 4.28106$ $B = 338.76$ $C = 104.97$
 Cox Constants $a = 0.93841$ $b = 1.74351 \times 10^{-3}$ $c = 8.43203 \times 10^{-7}$

Normal Boiling Point(B.P.) = $136.96^\circ\text{C} = 410.11^\circ\text{K}$

No.	Sample		Water		Pressure (mm.Hg.)	$\Delta t(^{\circ}\text{C})$ Antoine	$\Delta P(\text{mm.Hg.})$ Antoine	$\Delta P(\text{mm.Hg.})$ Cox
	emf. (mV)	t($^{\circ}\text{C}$)	emf. (mV)	t($^{\circ}\text{C}$)				
1.	2.3815	57.823	2.5365	61.316	158.79	-0.058	0.27	0.09
2.	2.6855	64.647	2.7245	65.515	191.99	-0.047	-0.24	0.07
3.	3.0195	72.019	2.9245	69.935	233.12	-0.053	-0.31	-0.80
4.	3.2505	77.044	3.0515	72.719	262.67	-0.043	0.26	-0.28
5.	3.4345	81.005	3.1515	74.898	287.95	-0.018	0.12	-0.37
6.	3.6415	85.419	3.2595	77.239	317.36	-0.018	0.12	-0.21
7.	4.1825	96.751	3.5225	82.887	398.90	-0.098	0.75	1.15
8.	4.6015	105.335	3.7135	86.944	467.73	-0.031	-0.26	1.35
9.	5.1715	116.763	3.9535	91.989	566.91	0.038	-0.35	1.39
10.	5.6585	126.312	4.1445	95.964	656.87	0.182	-1.74	-0.17
11.	6.0075	133.040	4.2695	98.547	721.44	0.078	-0.78	0.01
12.	6.1595	135.941	4.3225	99.637	750.24	-0.056	-0.57	-0.34
13.	6.3245	139.071	4.3775	100.766	781.06	-0.040	0.41	-0.13
14.	6.7705	147.435	4.5225	103.729	866.96	-0.171	1.82	-1.78

Std. Dev.

Antoine

Cox

P, mm.Hg.

0.82

t, $^{\circ}\text{C}$

0.082

 ΔH_v , Kcal g-mole $^{-1}$
 at B.P.

4.35

Cox Equation:

$$\Delta H_v = 2.302585 RT_b A_{\text{cox}} \quad (6)$$

where $\log A_{\text{cox}} = a + bT_b + cT_b^2$

Here T_b is the normal boiling point in °K.

The Antoine and the Cox constants for all compounds are reported in Table IX.

...

CONSTANTS OF THE ANTOINE AND COX VAPOR PRESSURE EQUATIONS

25

CHAPTER 6DISCUSSION AND CONCLUSION

The experimental method chosen in the present investigation has been demonstrated to give reliable vapor pressure measurements (12,25). Once the leaks were removed from the system, we found it rather simple to take the data which are both precise and accurate. Care was taken where necessary to use high purity samples, and to introduce sample and water into the system without exposure to air and moisture. One of the major problems faced in such studies is the procurement and availability of high purity samples. Our method of introducing the sample is not full-proof but is found to be quite satisfactory. Overall, the temperatures are accurate to ± 0.01 degree but in some cases the accuracy is not as good, because of the decomposition of the sample as discussed later. Provided the reference sample is very pure, this method of pressure measurement is very accurate. In the present investigation great care was taken to purify water and the errors in the temperature measurement due to impurities in water are expected to be less than 0.01° . This would give an error of less than 0.1 mm in pressure measurement.

For benzyl benzoate and nonyl phenol slight decomposition was observed as temperatures were increased. Hence at higher temperatures, fresh samples were charged for each point. In this manner the decomposition was minimized. The final

estimates of the accuracy of the present data for each compound are given in Table X.

Reliable data on these compounds are not available in the literature for comparison with our data. The comparison of older data with our values is shown in Table XI. In general the agreement around 760 mm Hg. pressure is satisfactory but the data deviate considerably at lower pressures. It is felt that the present data are closer to the "true" data than the older literature values.

TABLE XESTIMATED ACCURACIES OF VAPOR PRESSURE-BOILINGPOINT DATA

Compound	Approximate Purity, %	Maximum Uncertainty	
		Temperature °C	Pressure, mm Hg.
Benzyl benzoate	99.55	0.1	0.6
Bromoform	99.96	0.01	0.1
1-Bromonaphthalene	99.88	0.02	0.1
Cycloheptane	99.97	0.02	0.4
<u>n</u> -Nonanol	99.81	0.01	0.2
Nonyl phenol	99.83	0.04	0.4
Propylene Trimer	99.65	0.07	0.6

TABLE XI
COMPARISON OF PRESENT EXPERIMENTAL DATA WITH THE
LITERATURE VALUES

Benzyl Benzoate

Pressure mm. Hg.	Temperature, °C		Δt , °C
	Present	Ref.(15)	
59.4	216.27	220.0	3.73
709.0	319.46	320.0	0.54
760.0	323.25	323.5	0.25
867.0	330.63	330.0	-0.63

1-Bromonaphthalene

		Ref.(15)	
138.0	195.70	210.01	14.30
182.0	206.74	220.0	13.26
236.0	217.91	230.0	12.09
305.0	229.79	240.0	10.21
387.0	241.66	250.0	8.34
483.0	253.53	260.0	6.47
601.0	266.10	270.0	3.90
760.0	280.66	281.1	0.44
911.0	292.73	290.0	-2.73

Table Xi (continued)

<u>Bromoform</u>			
Pressure mm. Hg.	<u>Temperature, °C</u>		$\Delta t, ^\circ\text{C}$
	Present	Ref. (14)	
100.0	100.35	85.9	-14.45
200.0	115.21	106.1	- 9.11
400.0	131.78	127.9	- 3.88
760.0	148.63	150.5	1.87

<u>Nonyl Alcohol</u>			
Ref. (20)			
60.0	128.8	139.0	10.13
100.0	143.19	151.3	8.11
200.0	164.71	170.5	5.71
400.0	189.31	192.1	2.79
760.0	215.11	213.5	-1.61

NOMENCLATURE

A, B, C	Antoine Constants
a, b, c	Cox constants
B.P., BP	Normal Boiling Point
ΔH_v	Heat of Vaporization, Kcal/g.mole
P	Vapor pressure, mm Hg.
R	Gas constant, $R = 1.98717 \text{ cal. K}^{-1} \text{ g-mole}^{-1}$
T	Temperature, °K
T_b	Normal Boiling Point, °K
t	Temperature, °C
v_g	Molecular volume of gas phase
v_l	Molecular volume of liquid phase
x_B	Mole fraction of the impurity
Δ	Difference (Exptl-Calc.)

..

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APPENDIX A

THERMOCOUPLE CALIBRATION

A Sargent Thermonitor Controlled constant temperature bath ($\pm 0.01^\circ\text{C}$) and Ethylene Glycol (upto 130°C) and Maua Oil (upto 300°C) as bath fluids were used for the calibration purposes. The circuit diagram is shown in Fig.3. The hot junctions of thermocouples TC1 and TC2 were dipped to a depth of 15 cm in the constant temperature bath fluid and tied close to the Platinum resistance thermometer. The cold junctions were placed in dewar flasks containing a slurry of crushed ice and distilled water. Due caution was taken to avoid the formation of air pockets in the slurry. The calibration is given in Table XII. The measured data are correlated by means of the following equation:

$$E(\text{mV}) = a + bt + ct^2 \quad t^\circ\text{C} \quad (7)$$

The constant a, b, c were calculated by Rosenbrock Search analysis on IBM 7044 computer. The following "best" values were obtained:

$$a = 5.7889295 \times 10^{-3}$$

$$b = 3.7991025 \times 10^{-2}$$

$$c = 5.3526331 \times 10^{-5}$$

The function error of fitting $= 1.98 \times 10^{-4}$

For actual temperature measurement in the system, Fig. 4, Eqn.(7) was used.

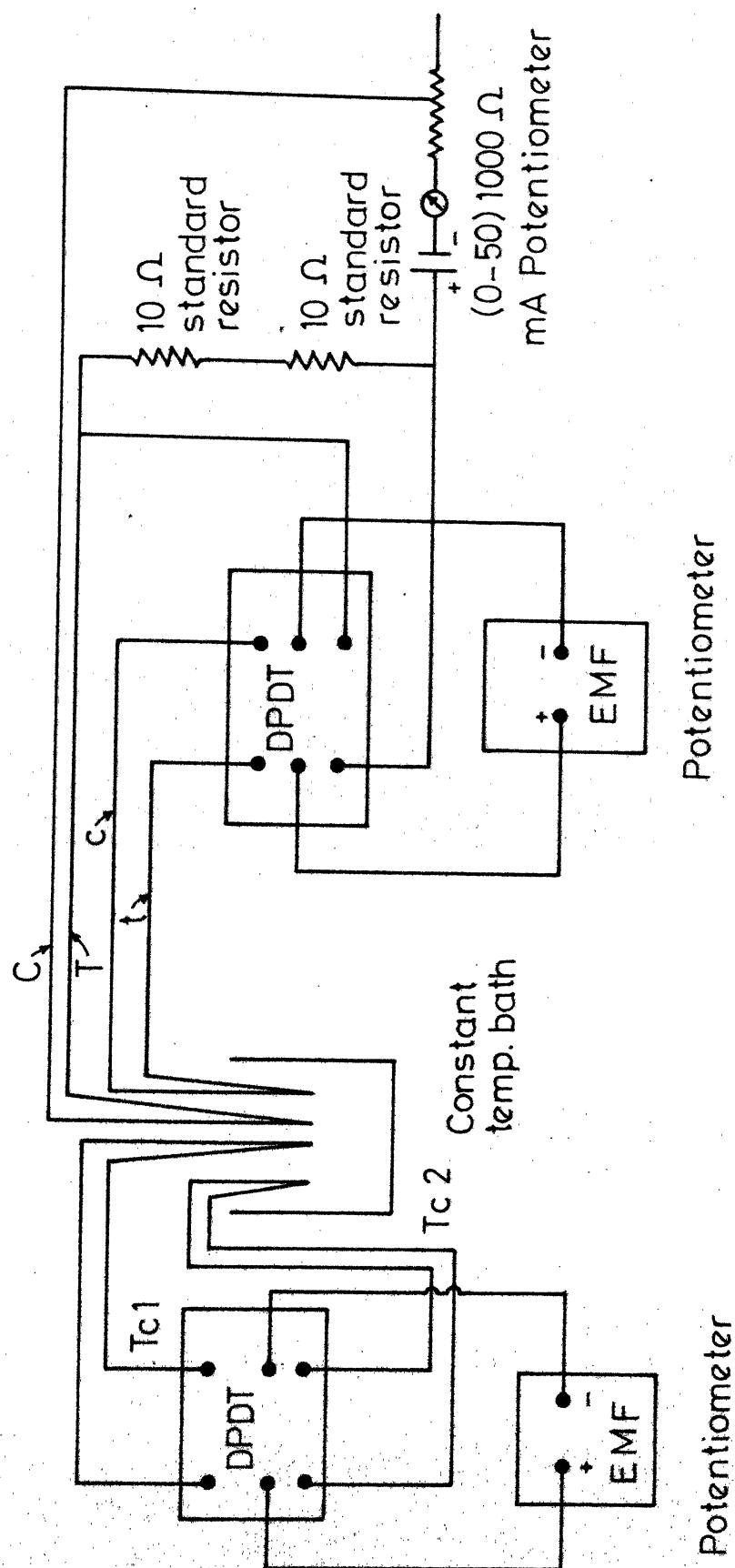


Fig. 3 - Thermocouple Calibration Circuit.

TABLE XII: CALIBRATION OF THERMOCOUPLES

Current: 2.99 mA

D.C. : 3.Volts

Reading No.	Thermocouple Reading emf (mV)	Current Radii	Temp., °C
1	1.04775	1.10282	25.888
2	1.40645	1.14157	35.698
3	1.49155	1.14874	37.519
4	1.63205	1.16159	40.781
5	1.86105	1.18177	45.908
6	2.04265	1.19746	49.901
7	2.29455	1.21979	55.594
8	2.48055	1.23720	60.038
9	2.74175	1.25883	65.568
10	3.17955	1.29759	75.500
11	3.63245	1.33609	85.399
12	4.67935	1.37168	94.574
13	4.78155	1.42092	108.962
14	6.30655	1.53343	138.726
15	7.32173	1.60417	157.583
16	9.11585	1.72224	189.304
17	10.1295	1.78550	206.433
18	12.1825	1.90708	239.613
19	15.8535	2.10639	294.776

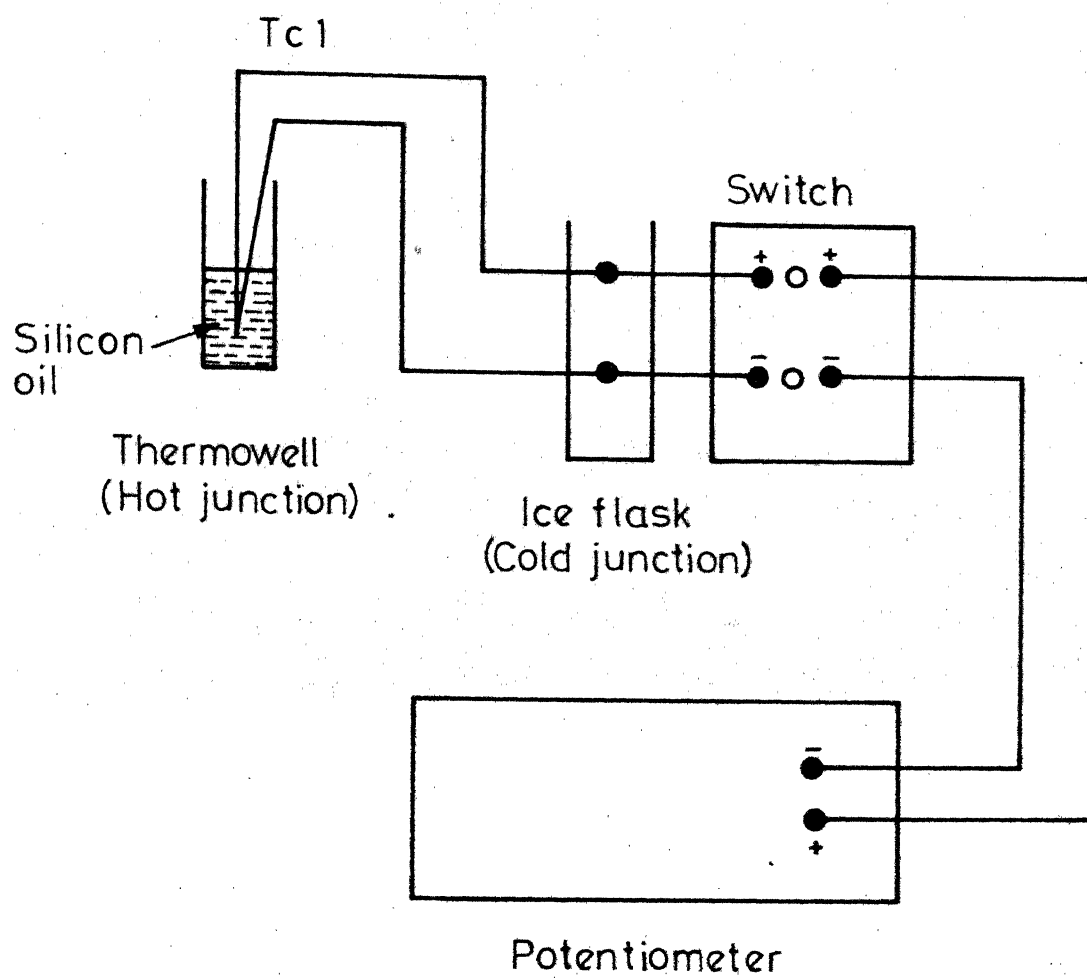


Fig. 4 - Temperature Measurement Circuit.

APPENDIX B

SCHEMATIC DIAGRAM OF THE PROGRAMME--(IBM-7044, IIT KANPUR)

```

*****
* START *
*****
*
*
*
*****
***
*
*****
* MAIN PROGRAMME--*
* INPUT DATA,*
* CALCULATION OF T,P---REQUIRES..*
* SUBROUTINES... TSAMPL AND EMFTEM.*
*****
*
*
*
*****
***
*
*****
* SUBROUTINE ANTOIN*
* CALCULATION OF ANTOINE CONSTANTS*
*****
*
*
*
*****
***
*
*****
* SUBROUTINE COX AND JANICE*
* CALCULATION OF COX CONTANTS*
*****
*
*
*
*****
***
*
*****
* SUBROUTINE MINIMY (FIG.5 FLOW-CHART ) *
* AND ***** STOP *
* SUBROUTINE... VECTOR, FUNXON, FERROR *
*****

```

MAIN PROGRAM

MAIN PROGRAM For calculation of Vapor Pressure-Temperature.

This program --- Requires Subroutines: TSAMPL & EMPTTEM .

SUBROUTINES

ANTOIN --- Calculation of Antoine constants.

COX --- Calculation of error from given Antoine and Cox constants.

FUNKON --- Function program for Antoine and Cox equations.

JANIC --- Calculation of error from given Cox constants.

MATINV --- Matrix inversion by the Gauss-Jordan method .

MINIMY --- Optimization method (Rosenbrock Search)
for Calc. Antoine and Cox constants.

VECTOR --- Calculation of variations .

ANTOIN AND COX ---Require Subroutine MATINV.

MINIMY ---Requires Subroutine VECTOR.

LIST OF NOTATIONS

<u>Symbols</u>	<u>Descriptions</u>	<u>Units or Equation</u>
ACS, BCS, CCS, and ACW, BCW, CCW	Constants of calibration of thermocouples for sample and water, respectively	$E = A + BT + CT^2$
AP	Approximate pressure reading from manometer	mm Hg.
DT1, DT2, DW	Derivative of T w.r.t. E for sample. 1 and 2, and water respectively.	T, °C
EMFS, EMFW, ESMP1, 2, and EW	Data from potentiometer reading for sample, 1, 2, and water	mV
N	Number of sets for experi- mental data	
N COMP	Number of compounds	
PNT1, PNT2	Letters in A-Format	
TITLE	Name of compound	
TSAMP2	Temperatures of samples calculated from equation:	$E = ACS + BCS.T +$ $CCS.T^2, T, °C$
1	Condensing temperature	
2	Boiling temperature	

...

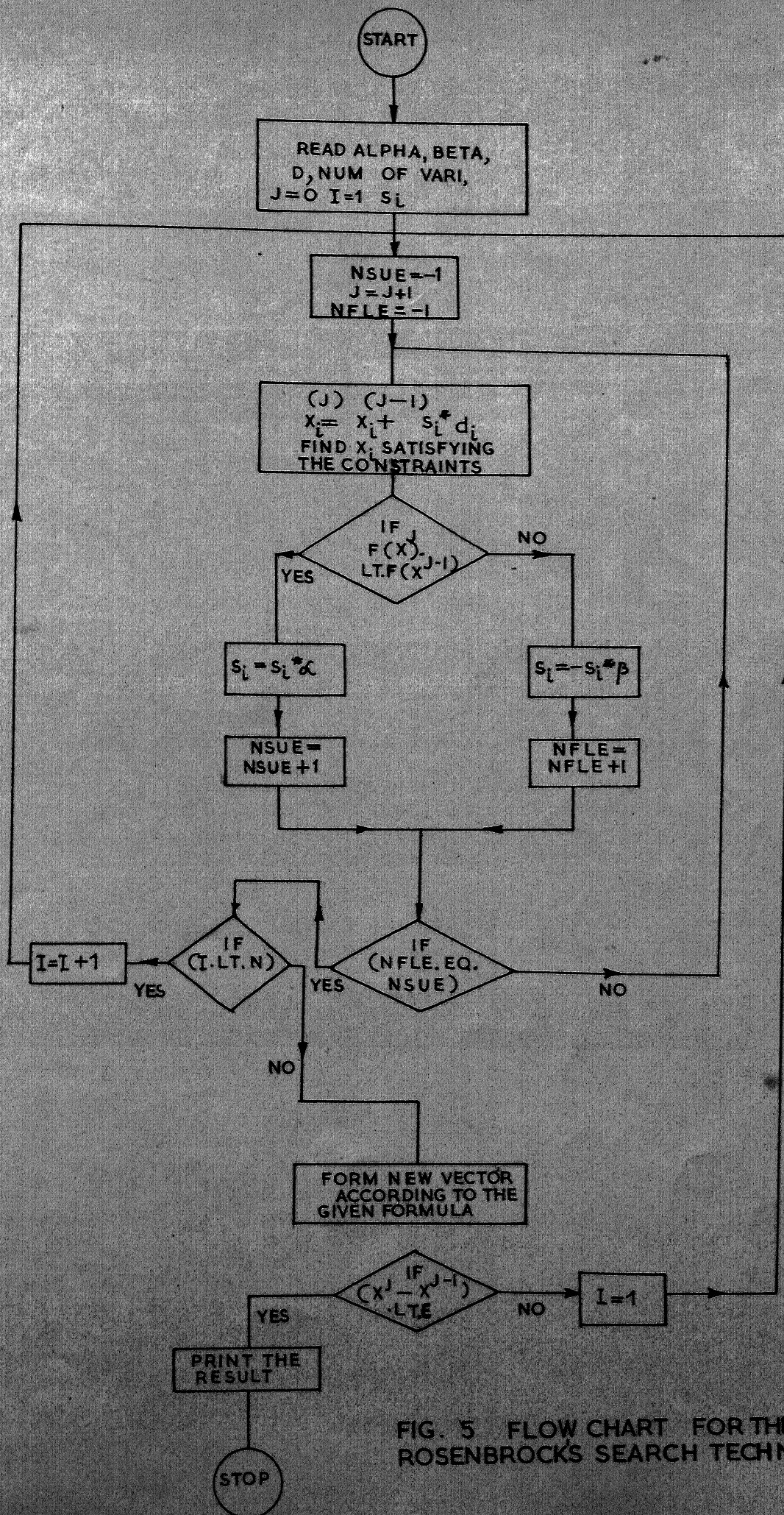


FIG. 5 FLOW CHART FOR THE
ROSEN BROCK'S SEARCH TECHNIQUE

\$IDJOB
\$IDFTC MAIN

C
C THE MAIN PROGRAMME FOR CALCULATION OF VAPOR PRESSURE-TEMPERATURE
C RELATIONSHIP

C THE MAIN PROGRAMME REQUIRES BELOW SUBROUTINE PROGRAMMES..
C TSAMPL AND EMFTM
C

C
C DIMENSION TITLE(30),EW(30),ESMP1(30),ESMP2(30),AP(30)
C DIMENSION DT1(30),DT2(30),DW(30)
C COMMON/JOHN/TSAMP2(30),PEXPTL(30)
C COMMON/JAMES/N
C COMMON/ANDER/EMFW(30),EMFS(30)
C PRINT OUTPUT FORMAT
50 FORMAT(1H1)
51 FORMAT(1X,131(1H*)/1X,1H*,2X,20A6,7X,1H*/1X,131(1H*))
52 FORMAT(2H *,28X,*S A M P L E*,42X,1H*,11X,*W A T E R F O R R E F (O F V
1P MMHG)*,5X,1H*/1X,131(1H-)/2H *, *NO P-OBS MMHG EMF MV 1 TCAL
2C 1 =T-ERROR 1 EMF MV 2 TCAL C 2 =I-ERROR 2*,1X,1H*,* EMF MV
3 TCAL C =T-ERROR PCAL MMHG =P-ERR *,1X,3H */1X,131(1H*))
53 FORMAT(A2,13,F9.3,F12.5,F12.5,F10.6,F12.5,F11.5,F10.6,1X,A2,F8.4,F
110.5,F8.5,F12.5,F8.5,A2)
54 FORMAT(1X,131(1H*)/1X,131(1HZ)/)
55 FORMAT(1X,1X,*FOR ERROR READING FROM POTENTIAL-METER E(MV)...*/
11X,* IF E .LEAST THAN 10. ...ERROR IS +- 0.0005*/
21X,* IF E .GREAT THAN OR EQUAL 10. ...ERROR IS +- 0.005*)
56 FORMAT(1X,1X,*STANDARD DEVIATION OF ERROR FOR...*/10X,*TEMPERATUR
1E FOR SAMPLE 1 =*,F12.5,* DEGREE C*/10X,*TEMPERATURE FOR SAMPLE 2
2 =*,F12.5,* DEGREE C*/10X,*TEMPERATURE FOR WATER(REF) =*,F12.5,*
3 DEGREE C*/10X,*--- THE ABOVE TABLE DATA TOOK FROM POTENTIAL-MET
4RE ---*)

C
C INPUT DATA
C READ 1,NCOMP
1 FORMAT(I2)
DO 11 ICO=1,NCOMP
READ 2,NM,(TITLE(I),I=1,NM)
2 FO-MAT(I3,12A6/,8A6)
READ 3,ACS,BCS,CCS
READ 3,ACW,BCW,CCW
3 FORMAT(3E15.8)
READ 4,N
4 FORMAT(I3)
READ 5,(EW(I),I=1,N)
READ 5,(ESMP1(I),I=1,N)
READ 5,(ESMP2(I),I=1,N)
5 FORMAT(8F10.6)
READ 6,(AP(I),I=1,N)
6 FORMAT(10F8.3)


```

      READ 7,PNT1,PNT2
7  FORMAT(2A2)
PRINT OUTPUT
  PRINT 50
  PRINT 51,(TITLE(I),I=1,NM)
  PRINT 52

```

STARTING CALCULATE ESAMPLE TO TEMPERATURES

```

SDTW=0.
SDTS1=0=
SDTS2=0=
SDTW=0.
DO 14 I=1,N
  ESM2=ESMP2(I)
  EF=EW(I)
  ESM1=ESMP1(I)
  CALL TSAMPL(ACS,BCS,CCS,TS1,DTS1,ESM1)
  CALL TSAMPL(ACS,BCS,CCS,TS2,DTS2,ESM2)
  CALL EMFTEM(ACW,BCW,CCW,EF,TW,P,DTW,DP)
  EMFW(I)=EF
  EMFS(I)=ESM2
  PEXPTL(I)=P
  TSAMP2(I)=TS2
  DT2(I)=DTS2
  DW(I)=DTW
  SDTS1=SDTS1+DT1(I)
  SDTS2=SDTS2+DT2(I)
  SDTW=SDTW+DW(I)
  PRINT 53,PNT1,I,AP(I),ESM1,TS1,DTS1,ESM2,TS2,DTS2,PNT2,EF,TW,DTW,P,
  DP,PNT1
CONTINUE
PRINT 54
PRINT 55

```

STANDARD DEVIATION

```

AVG1=SDTS1/FLOAT(N)
AVG2=SDTS2/FLOAT(N)
AVGW=SDTW/FLOAT(N)
SDMT1=0.
SDMT2=0.
SDMW=0.
DO 16 I=1,N
  SDMT1=SDMT1+(DT1(I)-AVG1)**2
  SDMT2=SDMT2+(DT2(I)-AVG2)**2
16 SDMW=SDMW+(DW(I)-AVGW)**2
STDNT1=SQRT (SDMT1/FLOAT(N))
STDNT2=SQRT (SDMT2/FLOAT(N))
STDNTW= SQRT (SDMW/FLOAT(N))
PRINT 56,STDNT1,STDNT2,STDNTW
CALL ANTOIN
CONTINUE
STOP
END

```


SIBFTC TSAMPL

C
C
C

CALCULATION OF TEMPERATURE FROM EMF(MV).. POTENTIO-METER READING

SUBROUTINE TSAMPL(AC,BC,CC,TS,DTS,ESM)

DELTA=SQRT (BC**2-4.*(AC-ESM)*CC)

TS=(-BC+DELTA)/(2.*CC)

DESM=0.5E-03

IF (ESM.GE.10.) DESM=0.5E-02

DTS=DESM/(BC+2.*CC*TS)

RETURN

END

SIBFTC EMFTEM

C
C
C
C

SUBROUTINE EMFTEM FOR CALCULATION OF VAPOR PRESSURE RELATIONSHIP ..
WATER..... ANTOINE EQUATION

SUBROUTINE EMFTEM(AC,BC,CC,EF,TW,P,DTW,DP)

DELTA=SQRT (BC**2-4.*(AC-EF)*CC)

TW=(-BC+DELTA)/(2.*CC)

DESM=0.5E-03

IF (EF.GE.10.) DESM=0.5E-02

DTW=DESM/(BC+2.*CC*TW)

C

IF (TW.GT.28.389) GO TO 1

AW=0.8184254E 01

BW=0.17913E 04

CW=0.23810E 03

GO TO 9

1 IF (TW.GT.39.886) GO TO 2

AW=0.81893986E 01

BW=0.1767262E 04

CW=0.23629E 03

GO TO 9

2 IF (TW.GT.49.215) GO TO 3

AW=0.80886767E 01

BW=0.1739351E 04

CW=0.23410E 03

```
CW=0.23410E 03
GO TO 9
3 IF (TW.GT.59.936) GO TO 4
  AW=0.80464202E 01
  BW=0.1715429E 04
  CW=0.23214E 03
  GO TO 9
4 IF (TW.GT.69.625) GO TO 5
  AW=0.80116295E 01
  BW=0.1695167E 04
  CW=0.23041E 03
  GO TO 9
5 IF (TW.GT.78.920) GO TO 6
  AW=0.79845588E 01
  BW=0.1678948E 04
  CW=0.22897E 03
  GO TO 9
6 IF (TW.GT.89.705) GO TO 7
  AW=0.79634288E 01
  BW=0.1665924E 04
  CW=0.22777E 03
  GO TO 9
7 IF (TW.GT.99.933) GO TO 8
  AW=0.79483960E 01
  BW=0.1656390E 04
  CW=0.22686E 03
  GO TO 9
8 AW=0.79186968E 01
  BW=0.1636909E 04
  CW=0.22492E 03
9 P=EXP(2.3026*(AW-BW/(CW+TW)))
  Dp=DTW*p*(BC/(CC+OW)**2)
  RETURN
END
```

SIBETC ANTOIN

SUBROUTINE ANTOIN

DIMENSION AT(30),LGP(30),ATCAL(30),LPCAL(10),ERR(30),EPT(30)

DIMENSION B(30),F(10,30),A(10,10),B(10,1)

DIMENSION BCOX(10,1),ACOX(10),ANTC(10)

COMMON/JOHN/T(30),P(30)

COMMON/JAMES/N1

COMMON/ANDER/EMFW(30),EMFS(30)

* REAL LPCAL,LGP

C PRINT OUTPUT

6 FORMAT(1X,1H17/1X,* THE VAPOUR PRESSURE --TEMPERATURE DATA F
1PERIMENTAL WORKS*/)

8 FORMAT(1X,128(1H-)/5X,*TEMP C OBS*,10X,**E OBS MMHG*,8X,*
1 *,10X,* A LOG10(P) EMF(MV)-WATER EM(MV)-SAMPLE*/1X,128

9 FORMAT(F15.3,F20.3,2F20.4,2F15.4)

100 FORMAT(1X,/1X,*CALCULATION OF ANTOINE COEFFICIENTS---*/)

110 FORMAT(10X,2HA=,F8.5,10X,2HB=,F9.3,10X,2C=,F8.3/)

120 FORMAT(1X,128(1H-)/1X,*TEMP(C)-OBS PRESSURE(MMHG)-OBS T
1 P(MMHG)-CAL DIF-T(CAL-OBS DIF(P(CAL-OBS) SLOP(P-T) H
2GML)*/1X,128(1H-))

130 FORMAT(F12.3,F21.3,F11.3,F13.3,F15.3,F15...F10.4,F13.3)

140 FORMAT(1X,100(1H-)/1X,*TOTAL ERROR OF PRESSURE =*,E20.8/1X,
1 ER-OR OF TEMPERATURE =*,E20.8/1X,*STANDARD DEVIATION OF ERR
2 PRESSURE =*,E20.8/1X,*STANDARD DEVIATION OF ERROR FOR TEMPE
3 **E20.8/1X,100(1H-)/1X,128(1H-))

151 FORMAT(1X,/1X,* N-BOL(LING TEMPERATURE **,F10.3,* DEG C**,
1BOL(LING T C) **,F12.3,* CAL/G-MOLESK)

146 FORMAT(1X,/5X,*COX EQUATION MODEL BY LEVYT SQUARES METHOD*/
147 FORMAT(1X,/5X,* OPTIMIZATION METHOD --COX MEDEL*/)

153 FORMAT(1X,12X,* HV **,F10.4,* CAL/G-MOLEAAT NORMAL BOILING P

C

PRINT 6

PRINT 8

DO 7 I=1,N1

AT(I)=1./T(I)

LGP(I)=ALOG10(P(I))

PRINT 9,T(I),P(I),AT(I),LGP(I),EMFW(I),EMFS(I)

7 CONTINUE

PRINT 100

DO 30 J=1,N1

F(1,J)=1.

F(2,J)=T(J)

F(3,J)=ALOG10(P(J))

```

      Y(J)=T(J)*ALOG10(P(J))
30  CONTINUE
      M=3
      DO 50 I=1,M
      DO 50 K=1,I
      A(K,I)=0.
      DO 60 J=1,N1
      A(K,I)=A(K,I)+F(I,J)*F(K,J)
60  CONTINUE
      A(I,K)=A(K,I)
50  CONTINUE
      DO 70 K=1,M
      B(K,1)=0.
      DO 70 J=1,N1
      B(K,1)=Y(J)*F(K,J)+B(K,1)
70  CONTINUE
      CALL MATINV(A,B,M,M,1,1)
      S=B(2,1)
      C=-B(3,1)
      V=-(B(2,1)*B(3,1)+B(1,1))
      PRINT 110,S,V,C
      PRINT 120
      DO 80 I=1,N1
      PCAL =EXP(2.302585*(S-V/(T(I)+C)))
      LPCAL(I)=ALOG10(PCAL)
      TCAL=V/(C-ALOG10(P(I)))-C
      ATCAL(I)=1./TCAL
      ERR(I)=PCAL-P(I)
      ERT(I)=TCAL-T(I)
      ANSLOP=2.3023*V/(T(I)+C)**2
      HV=1.987*ANSLOP*(T(I)+273.15)**2
      PRINT 130 ,T(I),P(I),TCAL,PCAL,ERT(I),ERR(I),ANSLOP,HV
80  CONTINUE
C TRYING FOR ERROR AFTER FITTING H. ANTOINE EQUATION MODEL
      SERR=0.
      SERR=0.
      DO 81 I=1,N1
      SER=SER+ERR(I)
81  SERR=SERR+ERT(I)
      AVCP=SERR/EDAT(N1)
      AVGT=SERR/EDAT(N1)
      SMP=0.

```

```

SMT=0.
DO 82 I=1,N1
  SMP=SMP+(ERR(I)-AVGP)**2
82 SMT=SMT+(ERT(I)-AVGT)**2
CALCULATION OF STANDARD DEVIATION OF P,T
STDNP=SQRT (SMP/FLOAT(N1))
STDNT=SQRT (SMT/FLOAT(N1))

PRINT 140,SEPP,SEPT,STDNP,STDNT

CALCULATION OF HEAT OF VAPORIZATION AT N- BOILING POINT
BPC=V/(S-ALOG10(760.))-C
HVNBT=1.987*2.3026*V*(BPC+273.15)**2/(C+PBPC)**2
PRINT 151,BPC,HVNB

CALCULATION OF ANTOINE CONSTANTS BY OTIMIZUUION METHOD
PRINT 145
145 FORMAT(1X,7/5X,* ANTOINE EQUATION MODEL 22 OPTIMIZATION METHOD*/ )
ANTC(1)=S
ANTC(2)=V*1.E-02
ANTC(3)=C*1.E-02
CALL MINIMY(ANTC,3)

PRINT 146
BP=V/(S-ALOG10(760.))-C+273.15
CALL COX(BCOX,BP,3)
SLNBP=2.3026*BP*EXP(2.3026*(B(1,1)+B(2,1)*BP+B(3,1)*BP**2))
HNBP=1.987*SLNBP
PRINT 153,HNBP
PRINT 147
ACOX(1)=BCOX(1,1)*10.
ACOX(2)=-BCOX(2,1)*1.E-03
ACOX(3)=BCOX(3,1)*1.E-07
ACOX(4)=BP*1.E-02
CALL MINIMY(ACOX,4)
RETURN
END

```


SUBROUTINE COX

```

SUBROUTINE COX(B,SP,MJI)
DIMENSION Y(30),F(10,30),A(10,10),B(10,1)
COMMON/JOHN/TEMP(30),P(30)
COMMON/JAMES/N
COMMON/HELEN/I(30)
120 PRINT(62X,'RESULTS',//57X,*B0= *,E15.8,/57X,*B1= *,E15.8,/
157X,*B2= *,E15.8,/57X,*B3= *,E15.8/57X,*B4= *,E15.8/57X,*B5=
2 *,E15.8/57X,*B6= *,E15.8/57X,*B7= *,E15.8/57X,*B8= *,E15.8/
3X,*B9= *,E15.8/57X,*B10= *,E15.8//)
DO 12 I=1,N
12 T(I)=TEMP(I)+273.15
C N IS NO. OF CONSTANTS
DO 13 M=3,MJI
C PRINT 40
DO 30 J=1,N
C EVALUATION OF FUNCTION
T(J)=ALOG10(ALOG10(P(J)/760.)/(1.-BP/T(J)))
C
T(1,J)=1.
DO 30 I=2,M
F(I,J)=T(J)**(I-1)
50 CONTINUE
DO 50 I=1,M
DO 50 K=1,I
A(K,I)=0.
DO 60 J=1,N
A(K,I)=A(K,I)+F(I,J)*F(K,J)
60 CONTINUE
A(I,K)=A(K,I)
50 CONTINUE
DO 70 K=1,M
B(K,1)=0
DO 70 J=1,N
B(K,1)=7(J)*F(K,J)+B(K,1)
70 CONTINUE
CALL MATINV(A,B,M,M+1,1)
PRINT 120,(B(I,1),I=1,M),BP
C CALCULATION OF ERROR
CALL JANICE(B,SP,M,F)
C
13 CONTINUE
RETURN
END

```

SIBFTC JANICE

SUBROUTINE JANICE(D,BP,M,F)
 DIMENSION D(10,1),F(10,30),DIFF(30)
 COMMON/JOHN/TEMP(30),P(30)
 COMMON/JAMES/N
 COMMON/HELEN/T(30)

PRINT 130

150 FORMAT(1X,128(1H-)/5X,*P(OBS) MMHG*,12X,*T(OBS) C*,8X,*P(CAL) MMHG
 1*,5X,*DIFF (CAL-OBS)*,7X,*LOG(ACOX)*,8X,*A-COX(T K)*,5X,*1/T(K)*,1
 2X,128(1H-))

SDP=0.

DO 80 J=1,N

DCAL=0.

DO 105 K=1,M

105 DCAL=DCAL+D(K,1)*F(K,J)

ACOX=EXP(2.3026*DCAL)

CB=(1.-BP/T(J))*ACOX

PCAL=760.*EXP(2.3026*CB)

DIFF(J)=PCAL-P(J)

SDP=SDP+DIFF(J)

ATK=1./T(J)

T(J)=T(J)-273.15

PRINT 140,P(J),T(J),PCAL,DIFF(J),DCAL,ACOX,ATK

140 FORMAT(7F18.6)

80 CONTINUE

AVGP=SDP/FLOAT(N)

SMP=0.

DO 75 J=1,N

75 SMP=SMP+(DIFF(J)-AVGP)**2

STDP=SQRT (SMP/FLOAT(N))

PRINT 142,AVGP,STDP

142 FORMAT(/75X,*AVERAGE OF DIF-P(CAL-OBS) =*,E20.8/5X,*STANDARD OF E
 IROR FOR PRESSURE =*,E20.8/1X,128(1H*))

RETURN

END

11010 MATINV

```

SUBROUTINE MATINV (A,B,NN,N,MM,M)
DIMENSION A(10,10),B(10,1),IPIVOT(20),PIVOT(20),INDEX(20,2)
LJ0=VALANCE (IROW,JROW),(ICOLUMN,JCOLUMN),(AMAX,T,SWAP)
10 DETERM=1.
15 DO 20 J=1,N
20 IPIVOT(J)=0
30 DO 550 I=1,N
C SEARCH FOR PIVOT ELEMENT
40 AMAX=0.0
45 DO 105 J=1,N
50 IF (+PIVOT(J)-1) 60,105,60
60 DO 100 K=1,N
70 IF (+PIVOT(K)-1) 80,100,740
80 IF (ABS(AMAX)-ABS(A(J,K))) 85,100,100
85 IROW=J
90 ICOLUMN=K
95 AMAX=A(J,K)
100 CONTINUE
105 CONTINUE
110 IPIVOT(ICOLUMN)=IPIVOT(ICOLUMN)+1
C INTERCHANGE ROWS TO PUT PIVOT ELEMENTS ON DIAGONAL
130 IF (IROW=ICOLUMN) 140,260,140
140 DETERM=-DETERM
150 DO 200 L=1,N
160 SWAP=A(IROW,L)
170 A(I=OW,L)=A(ICOLUMN,L)
200 A(ICOLUMN,L)=SWAP
205 IF(M) 260,260,210
210 DO 250 L=1,M
220 SWAP=B(IROW,L)
230 B(I=OW,L)=B(ICOLUMN,L)
250 B(ICOLUMN,L)=SWAP
260 INDEX(I,1)=IROW
270 INDEX(I,2)=ICOLUMN
310 PIVOT(I)=A(ICOLUMN,ICOLUMN)
C DIVIDE PIVOT ROW BY PIVOT ELEMENT
320 DETERM=DETERM*PIVOT(I)
330 A(ICOLUMN,ICOLUMN)=1.0
340 DO 350 L=1,N
350 A(ICOLUMN,L)=A(ICOLUMN,L)/PIVOT(I)
355 IF(M) 380,380,360
360 DO 370 L=1,M
370 B(ICOLUMN,L)=B(ICOLUMN,L)/PIVOT(I)
C REDUCE NON PIVOT ROWS
380 DO 550 LI=1,N
390 IF (LI=ICOLUMN) 400,550,400
400 T=A(LI,ICOLUMN)
420 A(LI,ICOLUMN)=0.0
430 DO 450 L=1,N
450 A(LI,L)=A(LI,L)-A(ICOLUMN,L)*T
455 IF(M) 530,550,460

```



```

460 DO 500 L=1,M
500 B(L1,L)=B(L1,L)-B(ICOLUM,L)*T
550 CONTINUE
C   INTERCHANGE COLUMNS
600 DO 710 I=1,N
610 L=N+1-I
620 IF(+NDEX(L,1)-INDEX(L,2)) 630,710,630
630 JROW=INDEX(L,1)
640 JCOLUM=INDEX(L,2)
650 DO 705 K=1,N
660 SWAP=A(K,JROW)
670 A(K,JROW)=A(K,JCOLUM)
700 A(K,JCOLUM)=SWAP
705 CONTINUE
710 CONTINUE
750 CONTINUE
740 RETURN
    END

```

IBFTC MINIMY

THIS SUBROUTINE PROGRAMME IS FOR MINMI-ERROR FUNCTION AND SIMULATANEOUS

PARAMETERS OF FUNCTION MODEL

SUBROUTINE MINIMY(X,N)

DIMENSION A(10,10),B(10,10),C(10,10),P(10,10),V(10,10),D(10),O(10)

1,R(10),X(10),Y(10)

COMMON/JOHN/TEM(30),PSV(30)

COMMON/JAMES/NK

DATA NS,MAXMIN,LIMIT,ALPHA,BETA,E,FL/20,1,1,3*0,0*5,0*00005,0*/

S=E

L=1

NSTAGE=-1

NTRIAL=-1

NSUXES=0

NFELUR=0

DO 1 I=1,N

D(I)=0.0

O(I)=X(I)

R(I)=0.0

Y(I)=0.0

DO 1 J=1,N

A(I,J)=0.0

B(I,J)=0.0

C(I,J)=0.0

P(I,J)=0.0

V(I,J)=0.

IF(J.EQ.I) V(I,J)=81.

1 CONTINUE

2 F=FUNXON(O,N)

IF(NTRIAL.LT.0) GO TO 9

IF(MAXMIN.EQ.0) GO TO 15

IF(LIMIT.EQ.0) GO TO 18

3 IF(F.LE.FM) GO TO 13

4 IF(NSTAGE.LT.0) GO TO 5

NFELUR=NFELUR+1

IF(NSUXES.GT.0) GO TO 21

5 E=-BETA*E

6 NTRIAL=NTRIAL+1

Y(L)=E

DO 8 I=1,N

O(I)=0.0

DO 7 J=1,N

7 O(I)=O(I)+5(I,J)*Y(J)

8 O(I)=O(I)+7(I)

GO TO 2

9 NTRIAL=NTRIAL+1

CALL FERROR(X,N,F)

13 FM=F

IF(NSTAGE.LT.0) GO TO 19

```

      Y(J)=T(J)*ALOG10(P(J))
30  CONTINUE
      M=3
      DO 50 I=1,M
      DO 50 K=1,I
      A(K,I)=0.
      DO 60 J=1,N1
      A(K,I)=A(K,I)+F(I,J)*F(K,J)
60  CONTINUE
      A(I,K)=A(K,I)
50  CONTINUE
      DO 70 K=1,M
      D(K,I)=0.
      DO 70 J=1,N1
      B(K,I)=Y(J)*F(K,J)+B(K,I)
70  CONTINUE
      CALL MATINV(A,B,M,M,1,1)
      S=B(2,1)
      C=-B(3,1)
      V=-(B(2,1)*B(3,1)+B(1,1))
      PRINT 110,S,V,C
      PRINT 120
      DO 80 I=1,N1
      PCAL=EXP(2.302585*(S-V/(T(I)+C)))
      LPCAL(I)=ALOG10(PCAL)
      TCAL=V/(S-ALOG10(P(I)))-C
      ATCAL(I)=1./TCAL
      ERR(I)=PCAL-P(I)
      ERT(I)=TCAL-T(I)
      ANSLOP=2.3026*V/(T(I)+C)**2
      HV=1.987*ANSLOP*(T(I)+273.15)**2
      PRINT 130 ,T(I),P(I),TCAL,PCAL,ERT(I),ERR(I),ANSLOP,HV
80  CONTINUE
C TRYING FOR ERROR AFTER FITTING H. ANTOINE EQUATION MODEL
      SERT=0.
      SERR=0.
      DO 81 I=1,N1
      SERR=SERR+ERR(I)
      SERT=SERT+ERT(I)
81  SERR=SERR/FLJAT(N1)
      AVGT=SERT/FLOAT(N1)
      SMP=0.

```

\$IBFTC VECTOR

SUBROUTINE VECTOR(A,B,C,P,V,D,R,N)

DIMENSION A(10,10),B(10,10),C(10,10),P(10,10),V(10,10),D(10),R(10)

DO 1 J=1,N

DO 1 I=1,N

DO 1 K=J,N

1 A(I,J)=A(I,J)+D(K)*V(I,K)

DO 2 I=1,N

B(I,1)=A(I,1)

2 R(1)=R(1)+B(I,1)**2

R(1)=SQRT(R(1))

DO 3 I=1,N

3 V(I,1)=B(I,1)/R(1)

DO 8 J=2,N

MJ=J-1

DO 4 K=1,MJ

DO 4 I=1,N

4 C(J,K)=C(J,K)+A(I,J)*V(I,K)

DO 6 L=1,MJ

DO 6 I=1,N

P(I,J)=P(I,J)+C(J,L)*V(I,L)

6 B(I,J)=A(I,J)-P(I,J)

DO 7 I=1,N

7 R(J)=R(J)+B(I,J)**2

R(J)=SQRT(R(J))

DO 8 I=1,N

8 V(I,J)=B(I,J)/R(J)

RETURN

\$IBETC FUNXON

```

      FUNCTION FUNXON(O,N)
      DIMENSION O(10),X(10)
      COMMON/JOHN/T(30),P(30)
      COMMON/JAMES/NK
      IF (N.EQ.3) GO TO 20
      DO 1 I=1,N
1  X(I)=O(I)
      AX1=X(1)*0.1
      AX2=-X(2)*1.E-03
      AX3=X(3)*1.E-07
      AX4=X(4)*1.E 02
      SUM=0.
C  DEFINATION FUNCTION
      DO 2 I=1,NK
      TK=T(I)+273.15
      ALGP=ALOG10(P(I)/760.)
      B=AX1+AX2*TK+AX3*TK**2
      A=10.**B
      C=A*(1.-AX4/TK)
2  SUM=SUM+(ALGP-C)**2
      FUNXON=SUM
      GO TO 26
20 A1=O(1)
      A2=O(2)*1.E 02
      A3=O(3)*1.E 02
      SF=0.
      DO 21 I=1,NK
21 SF=SF+(ALOG10(P(I))-(A1-A2/(T(I)+A3)))**2
      FUNXON=SF
26 RETURN
      END

```

SUBROUTINE ERROR

C THE SUBROUTINE PROGRAM FOR CALCULATION OF ERROR OF P AND T

SUBROUTINE ERROR(X,N,F)

DIMENSION X(10),DIFF(30),DIFT(30)

COMMON/JOHN/T(30),P(30)

COMMON/JAMES/NK

C PRINT OUTPUT

13 FORMAT(2F20.3,2F20.6)

15 FORMAT(1X,* PARAMETERS C =*,E16.8,* BOIL**G TEMP K =*,E16.8)

12 FORMAT(1X,/1X,128(1H-)/5X,*P (MMHG) OBS *5X,*TEMPERATURE C OBS

1*,5X,*PCAL MMHG *5X,*DIFF P(OBS-CAL)/1X,128(1H-))

14 FORMAT(1X,* FUNCTION ERROR =*,E16.8,* AVERAGE DIFF(OBS-CAL) =*,E16.8,* STANDARD DEVIATION P =*,E16.8,* MMHG*)

21 FORMAT(1X,* ANTOINE CONSTANTS C. A=*,F12.5,* B =*,F12.5,* C =*,F12.5)

25 FORMAT(1X,* FUNCTION ERROR =*,E16.8,* STD DEV. P =*,F12.5,* MMHG*,

1 STD DEV. T =*,F12.5,* DEG. C*)

IF (N.EQ.3) GO TO 20

AX1=X(1)*C.1

AX2=-X(2)*1.E-03

AX3=X(3)*1.E-07

AX4=X(4)*1.E-02

PRINT 15,AX1,AX2,AX3,AX4

C PRINT 12

DO 1 I=1,NK

TK=T(I)+273.15

C=AX1+AX2*TK+AX3*TK**2

A=10.**B

C=A*(1.-AX4/TK)

PCAL=760.*EXP(2.3026*C)

DIFF(I)=P(I)-PCAL

C PRINT 13,P(I),T(I),PCAL,DIFF(I)

1 CONTINUE

SDIFF=0.

DO 3 I=1,NK

3 SDIFF=SDIFF+DIFF(I)

AVDP=SDIFF/FLOAT(NK)

SMDPS=0.

DO 6 I=1,NK

6 SMDPS=SMDPS+(DIFF(I)-AVDP)**2

STDVNP=SQRT(SMDPS/FLOAT(NK))

PRINT 14,P,AVDP,STDVNP

```

GO TO 26
20 A1=X(1)
   A2=X(2)*1.E 02
   A3=X(3)*1.E 02
   PRINT 21,A1,A2,A3
   DO 22 I=1,NK
   PCAL=EXP(2.3026*(A1-A2/(A3+T(I))))
   DIFP(I)=P(I)-PCAL
   TCAL=A2/(A1-ALOG10(P(I)))-A3
22 DIFT(I)=T(I)-TCAL
   SDIFP=0.
   SDIFT=0.
   DO 23 I=1,NK
   SDIFP=SDIFP+DIFP(I)
23 SDIFT=SDIFT+DIFT(I)
   AVGP=SDIFP/FLOAT(NK)
   AVGT=SDIFT/FLOAT(NK)
   SMP=0.
   SMT=0.
   DO 24 I=1,NK
   SMP=SMP+(DIFP(I)-AVGP)**2
24 SMT=SMT+(DIFT(I)-AVGT)**2
   STNP=SQRT (SMP/FLOAT(NK))
   STNT=SQRT (SMT/FLOAT(NK))
   PRINT 25,F,STNP,STNT
26 RETURN
   END
ENTRY

```